

Millimeter wave analysis of the dielectric properties of oil shales

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Abstract

Natural sedimentation processes give rise to fine layers in shales. If these layers alternate between organic-rich and organic-poor sediments, then the contrast in dielectric properties gives rise to an effective birefringence as the presence of hydrocarbons suppresses the dielectric constant of the host rock. We have measured these effects with a quasioptical millimeter wave setup that is rapid and noncontacting. We find that the strength of this birefringence and the overall dielectric permittivity provide two useful diagnostic of the organic content of oil shales.

A common component of sedimentary rocks, kerogens are macromolecular compounds that are insoluble in light organic solvents. Kerogens are complex mixtures of organic components, primarily the result of the decomposition of algae deposited in fine-grained sediments under anaerobic conditions. Estimates of the recoverable hydrocarbons from kerogen-rich shales in Colorado alone range from 500 to 1500 billion barrels⁴ (i.e., around 10^{14} liters), so the economic importance of these oil-shales is considerable. Kerogens also play a role in discussions of the origin of life on Earth² as well as being possible signatures of life beyond Earth⁷.

The presence of alternating layers of kerogen-rich and poor layers in sedimentary rocks has a strong influence on the degree of electromagnetic birefringence. In the first part this paper we describe a study in which millimeter wave birefringence in oil-shale samples from a single borehole is measured. Our samples were taken from borehole #3 in the Roan Plateau of Western Colorado. Each sample was previously measured in bulk¹² for its oil-producing potential using the Fischer retort method (i.e., pyrolysis)⁹. We find that these two data sets are strongly correlated. Since the layering in the samples was on the order of a millimeter, millimeter waves (MMW) are a sensitive tool for studying this effect. Further, these measurements are rapid and completely non-contacting, making them straightforward to implement. To further explore the dielectric properties of shales, in the second part of this work, 8 additional samples had fine-scale Thermal Gravimetric Analysis (TGA) performed. These samples represent a wide variety of organic content. The results demonstrate that low dielectric constant (around 4.2 or less) is also a clear indicator of high organic content in oil shales.

At MMW frequencies, the propagation is via free space or waveguide. Our setup, a picture of which is shown in [11], is quasioptical. (See the book by Goldsmith⁶ for a thorough discussion of quasioptics (QO).) The measurements were performed with the MMW vector network analyzer (VNA) developed by AB Millimetre in Paris¹. The millimeter waves are generated by a sweepable centimeter wave source (i.e., microwaves; in this case from 8-18 GHz). For the lower frequency millimeter bands these centimeter waves are harmonically multiplied by Schottky diodes, coupled into waveguide and eventually radiated into free space by a scalar horn antenna. A polyethylene lens focuses the beam. At higher frequencies (beyond 170 GHz) high harmonics of the centimeter waves are phase locked to a separate Gunn source, which supplies the actual MMW power. In any case, a sample is placed in the

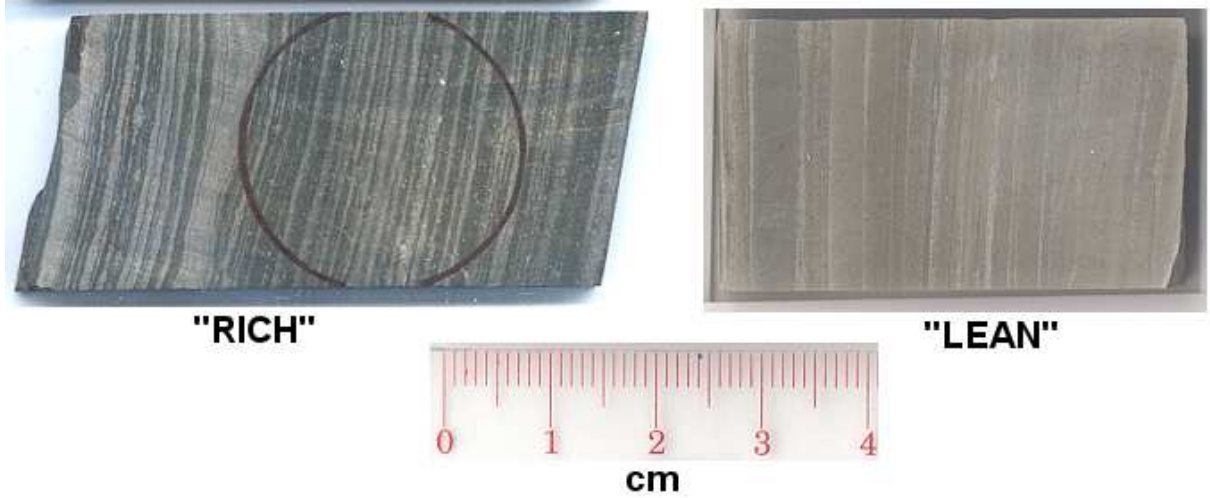


FIG. 1: Examples of the shale samples studied. Scale is in cm. The sample on the left has about 5 times the oil-yield potential as the one on the right. The geometrical layering is similar in the two cases, but the darker color is a clear indication of different chemical composition. The two samples were about 20 m apart in situ.

focal plane of the QO system.

The transmitted field is then collected by an identical lens/horn combination, detected by another Schottky harmonic detector and fed to a vector receiver which mixes the centimeter waves down to more easily manageable frequencies where the signal is digitized. Reflected waves are also collected by the transmitting horn and routed via a circulator and isolator to the vector receiver. The source and receiver local oscillators are phase-locked. The experiments described here were performed in the W band (nominally 75-110 GHz) and the H band (170-260 GHz); other bands are readily accessible by changing waveguides and sources/detectors. A more complete description of the system is given in [3, 10, 11].

Figure 1 shows two of the five shale samples used in the birefringence measurements. On the left is shown a vertical section through sample number 552. The circle denotes the size of the piece that was cut to fit in the optical mount. On the right is another sample of the same formation but from approximately 20 m deeper in the well. For each of the five samples, 25 mm diameter by approximately 5 mm thick cylinders were cut to fit into a rotational optical mount.

When the samples are cut in the direction of the layering, so that the transmitted MMW see, in effect, a grating structure, we can think of the sample as a uniaxial crystal with

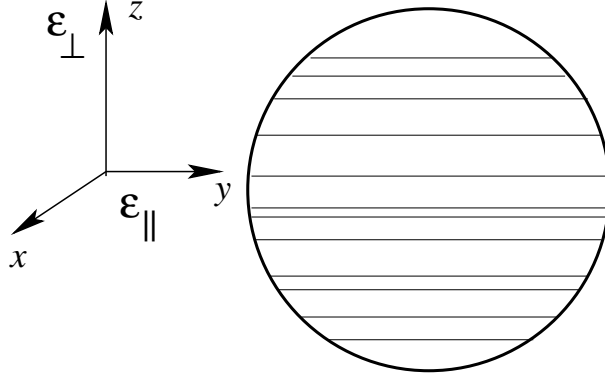


FIG. 2: We model the finely layered samples as a homogeneous, uniaxial birefringent media. The optical axis is perpendicular to the layering. In the results shown in Figure 4, 0 degrees corresponds to having the optical axis in the vertical (z) direction.

optical axis perpendicular to the layering as shown in Figure 2. Uniaxial crystals have only two independent dielectric tensor components⁸. The element along the optical (z) axis will be denoted by ϵ_{\perp} (because the optical axis is perpendicular to the layering) the elements in the $x - y$ plane are equal and will be denoted ϵ_{\parallel} . This is the notation used by Goldsmith [6, page 201]. Beware that this is the opposite of the notation used by Landau and Lifshitz in [8], who regard ϵ_{\parallel} as being parallel to the optical axis.

In our measurements the frequencies used (110-270 GHz) correspond to wavelengths in the range of 2.7mm to 1.1mm in free space. The layers are on the order of a millimeter or less. To get a quantitative estimate of the spatial distribution of the layers we converted the optical scan in Figure 1 into zeros and ones and simply made histograms of the corresponding distributions. First the two-dimensional (2D) scan was converted into a binary image (cf. Figure 3). Then this 2D binary image was converted to 1D by averaging along the layers. Finally, this was again converted into zeros and ones to give a binary sequence (kerogen-rich, kerogen-poor). Then it is a simple matter to calculate the thickness of all the layers and make histograms of these thicknesses for the two types of material. Given the complexity of the samples this procedure should be taken as a very approximate analysis. Nevertheless, we obtain estimates of 1 mm for the average kerogen-rich layers and .5 mm for the kerogen-poor layers.

Figure 4 shows measurements of the phase of the transmitted electric field through two of the five samples. Our measurement uses a single-mode (TE₁₀) Gaussian beam polarized

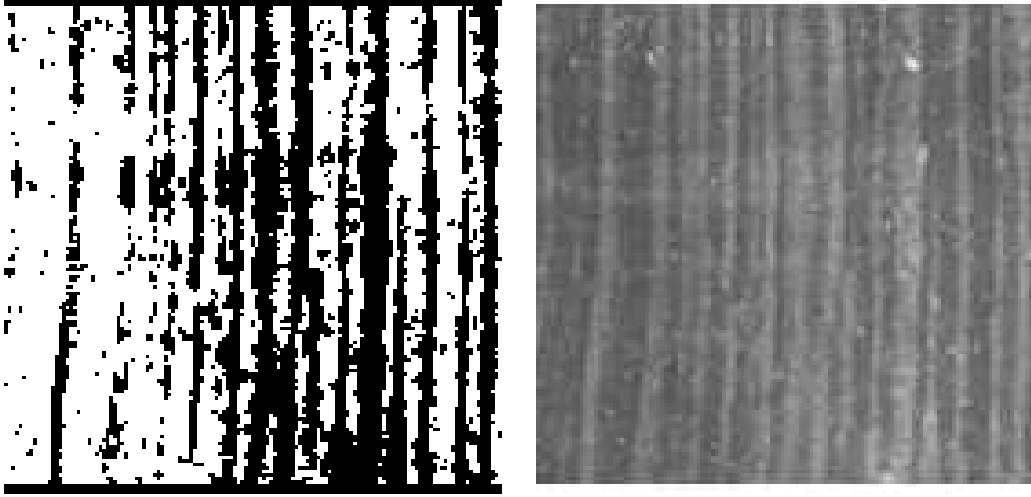


FIG. 3: A 25mm by 25mm scan of the oil-rich sample 552 (right) and a binary version (left) used for statistical analysis. Histograms of the data at this threshold level suggest that the typical kerogen-rich layer is about 6 pixels thick (about 1mm) and a typical kerogen-poor layer is about 3 pixels thick (about .5 mm).

vertically, i.e., along the optical axis when the samples are at 0 degrees and is normally incident on sample. The phase of the electric field can be read off the VNA directly. At a given frequency there are no apparent angle-dependent amplitude effects.

We've chosen to show the data in Figure 4 in terms of the phase of the E field to emphasize the fact that this is what we measure directly. However, this phase also depends on the thickness of the sample, which varies slightly from sample to sample. So in Figure 4 a small correction has been applied to remove this effect. Henceforth, we will relate angle-dependent phase to angle-dependent index of refraction (a size-independent material property) via $\delta\phi = \frac{2\pi d}{\lambda}\delta n$ where $\delta\phi$ is the difference in the transmitted phase (in radians) between the two measurements of the E field, parallel to and perpendicular to the optical axis, δn the corresponding change in index, d is the thickness of the sample and λ the wavelength.

As shown in Figure 4, there is a strong correlation between kerogen content and the degree of MMW birefringence. The possibility that we could use this birefringence to infer organic content led us to measure three more samples distributed though the same borehole but with different kerogen levels. Figure 5 shows the results of MMW birefringence measurements for all five initial samples. The data are plausibly consistent with a straight line having a

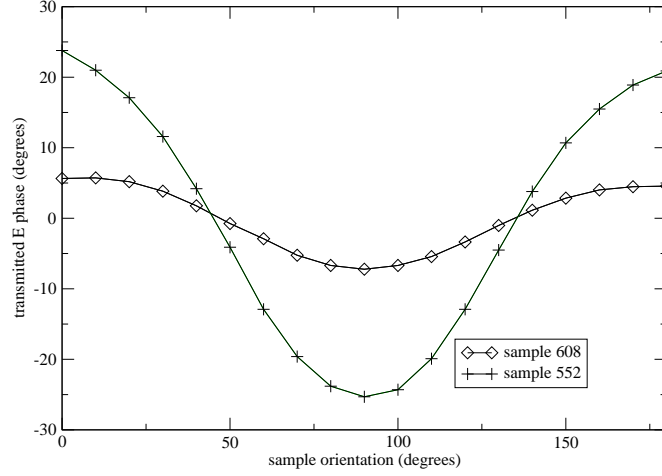


FIG. 4: Birefringence in the transmitted E field as measured with the VNA at 110 GHz (2.7 mm wavelength). 0 degrees corresponds to the E field parallel to the optical axis. By previous chemical analysis, sample 552 has 5 times the organic content of sample 608.

slope of 28 liters/1000 kg per .01 increase in the birefringence; the latter being defined as the difference in the index of refraction between 0 degrees (E polarized parallel to the optical axis) and 90 degrees (E perpendicular to the optical axis).

The kerogen itself appears to have little intrinsic birefringence. We took the sample with relatively high kerogen content (241 liters/1000 kg) and cut a 25mm diameter by 6.8 mm thick cylindrical sample so that the layers were along the axis of the cylinder and so that the sample consisted almost entirely of the kerogen rich shale component. The birefringence was .004. This is far smaller than that measured for any of the samples cut with the layering perpendicular to the optical axis. The real part of the dielectric permittivity for this kerogen-rich sample was 4.2 ($n = 2.05$) The same measurement from one of the most kerogen-poor sample gave a permittivity of 5.4 ($n = 2.3$).

Because the wavelengths used were comparable to the layer thicknesses, there is strong frequency dependence of the birefringence. To reach higher MMW frequencies we used a Gunn oscillator extension of the VNA to span the H band and get the birefringence in the range of 170 GHz to 260 GHz. The results are shown in Figure 6. We can see that the birefringence increases with frequency and is extremely strong at 260 GHz in the kerogen rich sample. At 260 GHz the wavelength in free space is only 1.1 mm, while in the shales it

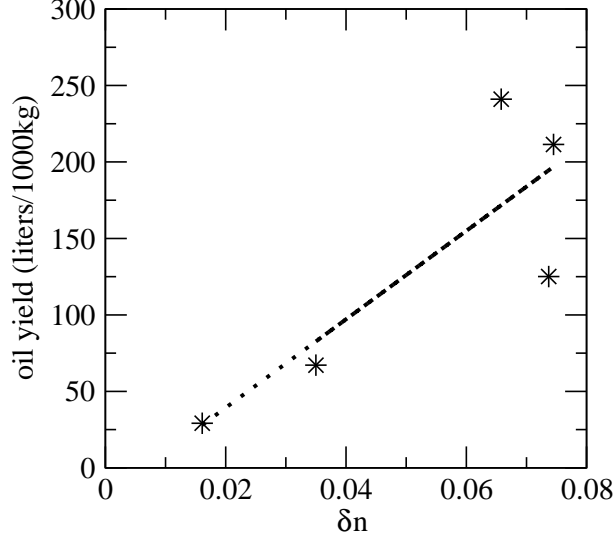


FIG. 5: Birefringence in all the oil-shale samples measured with the VNA at 110 GHz (2.7 mm wavelength). The plot shows oil-yielding potential (known from previous analysis) plotted against the measured birefringence in the index of refraction. Here δn is the difference between the index at 0 and 90 degrees respectively. As a point of reference, the birefringence of crystalline quartz is about .047 at the same frequency, while for sapphire it is .34⁶.

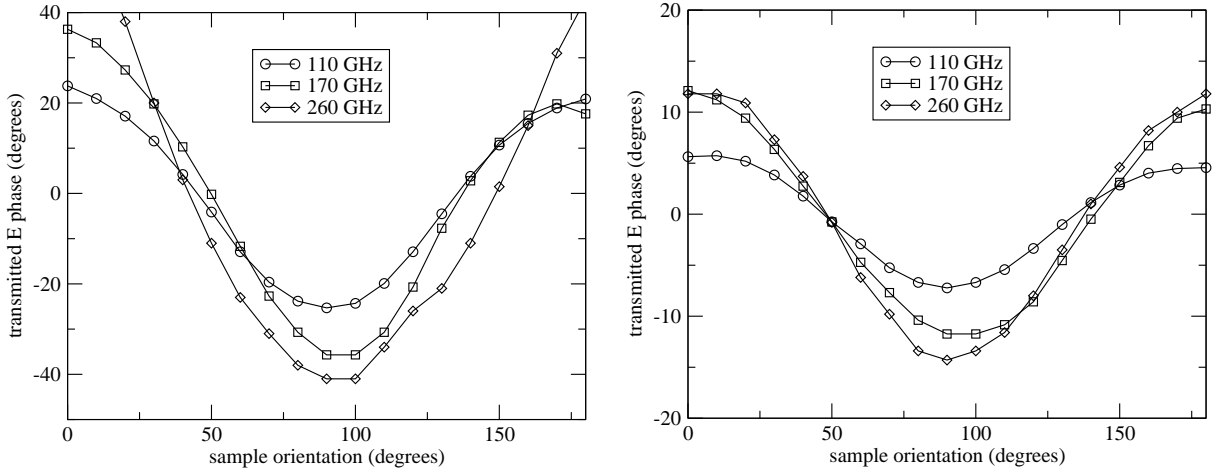


FIG. 6: Measured birefringence of the samples 552 (left) and 608 (right) over both W and H band.

is about half that. That makes the MMW approximately resonant with the layers.

Even in the absence of layering-induced birefringence, the dielectric constant itself is a good indicator of the organic content of the shales. Oil itself has a very low index of refraction (about 1.5)¹¹. This is much lower than the host rock and hence kerogen rich

samples will tend have a lower permittivity than kerogen poor samples. This can lead to counterintuitive results for geologists, who, in the field, rely on the color of the sample as an indicator of hydrocarbons. Dark samples are assumed to have more oil. But our results show that this can be misleading. For example, we looked at samples from an outcrop that had been visually classified as having high oil yield potential. However, they showed no birefringence and the highest dielectric constant of any of the samples we have measured thus far, 6.35, which would suggest an absence of kerogen.

To investigate this issue further we took an assortment of 8 samples believed to have widely varying organic content, measured their dielectric properties and performed Thermal Gravimetric Analysis (TGA)⁵. TGA is similar to the classic retort method, but more accurate and able to utilize much smaller samples. At about 450 C any hydrocarbons will burn off giving rise to a significant change in mass. The results are shown in figure 7. The horizontal axis is the temperature in Celsius and the vertical axis is the mass change with temperature (dM/dT) as a percentage of the total mass of the sample. The correlation between low permittivity and high kerogen yield (associated with a high peak at about 450C in the TGA curves) is quite clear. In the case of samples *112.1 rich* and *112.1 lean*, these were thin (1-2mm) layers cut from the interior of individual layers in a laminated sample. The “lean” sample being light colored and the “rich” sample being dark.

In conclusion we have shown that the dielectric properties of shales are clear indicators of their organic content and that these properties are easily and rapidly measured with a non-contacting millimeter wave setup. We believe that millimeter wave dielectric spectroscopy will be a valuable tool in the nondestructive analysis of organic content in natural materials.

Acknowledgments

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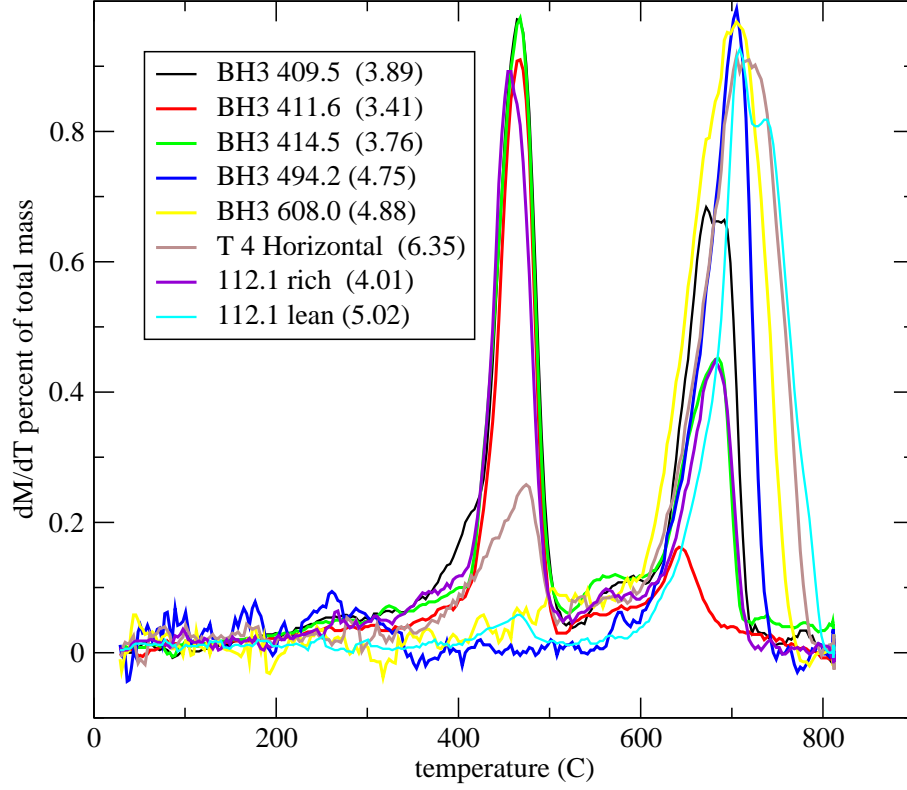


FIG. 7: Thermal gravimetric analysis (TGA) of 8 samples. The real part of the dielectric constant is shown in parantheses in the legends. For oil rich (and hence birefringent) samples, $\epsilon_{||}$ is shown. TGA is essentially a modern retort analysis. Small samples are heated and weighed simultaneously. The peak at 450C is due to the breakdown of the kerogens, while the peak at around 700C is likely due to breakdown minerals such as calcite, dolomite and ankerite.⁵.

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